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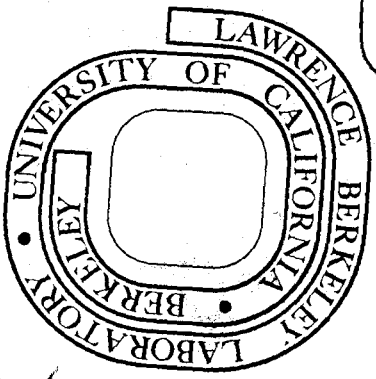
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GEOMETRY OF THE LiO_2 RADICAL[*]

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ABSTRACT

<u>Ab initio</u> quantum mechanical calculations have been carried out for the

two lowest electronic doublet states of the lithium dioxide molecule. The

results are pertinent to possible crossed molecular beam experiments and to

matrix isolation spectroscopy. A qualitative discussion of the electronic

structure changes accompanying the $Li + O_2$ and $LiO + O$ reactions is given. For

the quantitative calculations, a contracted gaussian basis set was used, des-

ignated Li (9s 4p/4s 2p), O (9s 5p/4s 3p). For isosceles triangle configurations,

the $^2A_2$ state is the electronic ground state, with equilibrium geometry r(LiO) =

1.82 Å and θ(O-Li-O) = 44.5°. The $^2B_2$ state is predicted to lie 14 kcal/mole

higher with r(LiO) = 1.76 Å, and θ(O-Li-O) = 46.5°. For $C_{\infty v}$ geometry the $^2\Pi$ state

bond distances were predicted, R (Li-O) = 1.62 Å and R(O-O) = 1.35 Å. There

appears to be little or no barrier between the C_{2v} and $C_{\infty v}$ forms.

INTRODUCTION

Recent developments in the experimental study of chemical reactions using crossed molecular beams have produced an impressive amount of detailed information on the dynamics of an increasing number of interesting reactions.[1] An interesting reaction which has not been studied is

$$Li + O_2 \longrightarrow LiO + O \quad .$$
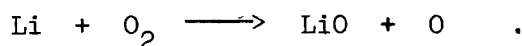
While O_2 beams are relatively easy to prepare, only within the past several years have reactions involving Li been observed in crossed beams.[2] However, the real reason the Li + O_2 reaction has not been studied is the endothermicity involved, ~37 kcal/mole.[3] In principle, of course, this endothermicity could be overcome either by giving the reactants excess (relative to thermal energies) kinetic energies or by vibrationally exciting the O_2 molecules, or by some combination of the two. In practice, however, either of these two routes appears rather difficult. In fact, the exothermic reverse reaction appears a more likely candidate for beam studies, even though both LiO and O would be difficult to prepare in beams. Furthermore, the reverse reaction might be more interesting since the $v = 0$ through $v = 12$ vibrational states of O_2 are energetically accessible.[4]

The dynamics of the Li + O_2 and LiO + O reactions will of course depend on the potential energy surfaces which correlate with the reactants. For Li(^2S_g) + O_2 ($^3\Sigma_g^-$) and $C_{\infty v}$ geometries, $^4\Sigma^-$ and $^2\Sigma^-$ states of LiOO are possible. For C_s geometries $^4A''$ and $^2A'$ states of Li$_{\diagdown O-O}$ can arise, and for C_{2v} geometries, the pertinent potential surfaces of $_O\diagup^{Li}\diagdown_O$ are $^4B_1$ and $^2B_1$. These are the three types of geometries at which a Li atom can approach an O_2 molecule. For the LiO($^2\Pi$) + O(^3P_g) reaction, a larger number of surfaces are accessible due to the spatial

degeneracy of the reactants. Specifically, for $C_{\infty v}$ approaches the $^4\Sigma^+$, $^4\Sigma^-$, $^4\Pi$, $^4\Delta$, $^2\Sigma^+$, $^2\Sigma^-$, $^2\Pi$, and $^2\Delta$ surfaces will be accessible. For general geometry (C_s), the pertinent surfaces will be $^4A'$ (3), $^4A''$ (3), $^2A'$ (3), and $^2A''$ (3). As discussed by Herzberg,[5] there is not a unique symmetry-determined correlation between $^2\Pi$ LiO + ^3P O and the C_{2v} electronic state of LiO_2. There will be 12 such C_{2v} potential surfaces, and they may be of any of the symmetries $^4A_1$, $^4A_2$, $^4B_1$, $^4B_2$, $^2A_1$, $^2A_2$, $^2B_1$, and $^2B_2$. Since these 12 surfaces must correlate with the C_s surfaces designated above, there will be no more than three C_{2v} surfaces of the same irreducible representation. The precise correlation between C_s and C_{2v} states can only be obtained by solving the electronic Schrödinger equation.

The above discussion shows that the Li + O_2 reaction proceeds on two potential energy surfaces, while the LiO + O reaction can occur on 12 different surfaces. It seems clear that a detailed _a priori_ description of the two reactions would be difficult to obtain. Therefore, in the present work we have set for ourselves a much more modest goal: to learn something about only the lowest two potential surfaces of LiO_2 near their equilibrium geometrical configurations. Such information will of course be qualitatively pertinent to crossed molecular studies. If LiO_2 is significantly bound with respect to LiO + O, one may expect long-lived collision complexes to accompany the reactions. Otherwise the reactions may be expected to proceed in a "direct" fashion, resulting in little forward and backward peaking in the angular distribution.[6]
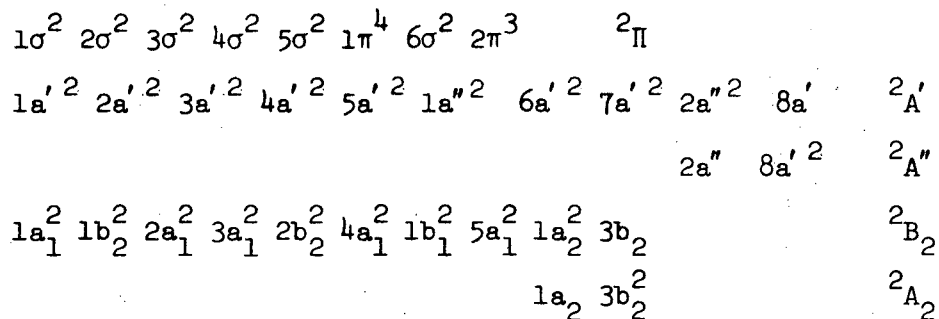
The LiO_2 radical has been observed experimentally by Andrews and coworkers[7] in low temperature oxygen and noble gas matrices. They have concluded that the bonding is ionic, $Li^+ O_2^-$, and hence that the proper name for the molecule should be lithium superoxide. In addition Andrews was able to classify the equilibrium

geometry of LiO_2 as an isosceles triangle, point group C_{2v}. Finally, they

estimated the Li-O bond distance to be 1.77 Å and the $\overset{\displaystyle Li}{\underset{\displaystyle O \quad O}{\diagup \backslash}}$ bond angle to be 44°.

The only previous theoretical work on LiO_2 appears to be that of

Billingsley and Trindle.[8] They used a "mixed basis set", with simple integrals

being evaluated over Slater functions, and the more difficult integrals by gaussian

expansions of the Slater functions. Constraining the molecule to be of C_{2v}

symmetry, Billingsley and Trindle[8] obtained good agreement with the experimentally

estimated geometry.[7] However, they predicted the equilibrium geometry not to be

a C_{2v} but rather a C_s structure with $\overset{\displaystyle Li}{\underset{\displaystyle O-O}{\diagdown}}$ bond angle of about 135°. This type

of geometry is qualitatively similar to that predicted earlier for the HO_2

radical.[9] For LiO_2, however, this disagreement between calculation and experiment

is disturbing. Billingsley and Trindle suggest several reasons why the matrix-

isolation identification of the molecule as C_{2v} at equilibrium might be incorrect.

LOW-LYING ELECTRONIC STATES OF LiO_2

If one assumes the electronic ground state of the lithium superoxide molecule to have the structure $Li^+O_2^-$, then the $C_{\infty v}$ symmetry will be $^2\Pi$, the C_s symmetry either $^2A'$ or $^2A''$, and the C_{2v} symmetry either $^2A_2$ or $^2B_2$. The corresponding electron configurations will be

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 1\pi^4\ 6\sigma^2\ 2\pi^3 \qquad ^2\Pi$$

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 1a''^2\ 6a'^2\ 7a'^2\ 2a''^2\ 8a' \qquad ^2A'$$

$$2a''\ 8a'^2 \qquad ^2A''$$

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 1b_1^2\ 5a_1^2\ 1a_2^2\ 3b_2 \qquad ^2B_2$$

$$1a_2\ 3b_2^2 \qquad ^2A_2$$

It is interesting to note that for $C_{\infty v}$ and C_{2v} approaches, $Li(^2S_g)+O_2(^3\Sigma_g^-)$ does <u>not</u> correlate with the assumed electronic ground state of LiO_2. This is because, as discussed in the introduction, the ground state reactants correlate with the $^4\Sigma^-$ and $^2\Sigma^-$ states of linear LiO_2 and the $^4B_1$ and $^2B_1$ states of the isosceles molecule. However, it is clear that essentially all $Li + O_2$ collisions will occur for C_s geometries, and $Li(^2S_g) + O_2(^3\Sigma_g^-)$ does correlate with the $^2A''$ state, which should be either the ground or first excited state in the ionic picture. For the reverse reaction $LiO + O$, the large number of accessible surfaces makes possible the correlation with either of the two lowest states of LiO_2 for all three point groups.

One would like to be able to predict the geometry of LiO_2 on the basis of Walsh-like arguments.[10] Although it might appear that a Walsh diagram for AB_2 triatomics would be useful for this purpose, the usefulness is limited. The diagram can be used to predict that for C_{2v} geometries the $^2B_2$ state should lie slightly below the $^2A_2$ state. This is done by noting that, of the a_2 and b_2 components of the $1\pi_g$ orbital (which is triply occupied in O_2^-), the a_2 lies

lower for C_{2v} geometries. Hosever, the absence of a doubly occupied 2s orbital in the Li atom makes Walsh's diagram otherwise inapplicable. That is, it appears that BO_2 is the simplest dioxide molecule for which Walsh's diagram is applicable. Taken literally, the AB_2 diagram predicts LiO_2 (13 valence electrons) to be linear, of $D_{\infty h}$ symmetry. A perhaps more reasonable possibility is to use the HAB Walsh diagram, neglecting the core 1s orbital of lithium. In this case LiO_2 is predicted to have the same geometry as HO_2,[9] about 105°. As is the case for HO_2, Walsh's diagram predicts the $^2A''$ state of LiO_2 lie below the $^2A'$ state. In this regard it should be noted that Gole and Hayes[11] have predicted the $^2A'$ state of HO_2 to lie only 17 kcal above the $^2A''$ ground state.

DETAILS OF THE CALCULATIONS

A basis set of contracted gaussian functions was employed in the present work. For lithium, the (9s 4p) primitive gaussian basis of Huzinaga[12] and Williams[13] was contracted to (4s 2p) in the spirit of Dunning's work.[14] For oxygen atom, the basis used was the Huzinaga-Dunning (9s 5p/4s 3p) set. Although we frequently use the less flexible 2p contraction of oxygen p functions, in the present work the 3p set was used to provide a better description of possible ionic $Li^+ O_2^-$ bonding. In summary, then 69 primitive gaussian functions were contracted to 36 functions.

Open-shell self-consistent-field calculations[15] were carried out for the lowest $^2A'$ and $^2A''$ states of LiO_2. In employing only a single plane of symmetry in constructing molecular orbitals from the chosen basis functions, we have exploited only that element of symmetry which is common to the three point groups $C_{\infty v}$, C_s, and C_{2v}. Within the single configuration SCF framework,[16] this is the only way to avoid discontinuities in the calculated potential energy surface. Recall that for $C_{\infty v}$ geometries the $^2A'$ and $^2A''$ states are the degenerate components of the $^2\Pi$ state, while for C_{2v} geometries $^2A'$ becomes $^2B_2$ and $^2A''$ becomes $^2A_2$. However, when the individual molecular orbitals are forced to have full C_{2v} summetry, the $^2B_2$ energy is calculated to lie ~ 0.003 hartrees = 2 kcal/mole above the energy obtained imposing only C_s symmetry. This perhaps somewhat surprising result is due to the fact that, for the type of wave function chosen, the spatial symmetry of the electronic state being described represents a (slight) constraint on the wave function. Removal of this constraint yields a slightly lower restricted Hartree-Fock energy.

GEOMETRIES

Assuming the molecule to have an isosceles triangle structure, the SCF energy of the $^2B_2$ and $^2A_2$ states was first minimized with respect to the bond distance R(Li-O) and bond angle Θ (O-Li-O). Next a $C_{\infty v}$ geometry was assumed and the energy minimized with respect to R(Li-O) and R(O-O). As mentioned earlier, the lowest $^2A'$ and $^2A''$ states are degenerate components of the $^2\Pi$ state for $C_{\infty v}$ geometries. All these results are summarized in Table I. Also included in Table I are the calculations of Billingsley and Trindle[8] and the experimental estimates of Andrews.[7]

The present _ab_ _initio_ self-consistent-field calculations predict the $^2A_2$ state to lie 14 kcal/mole below the $^2B_2$ state. The two states have very similar equilibrium geometries. Both of the above facts are quite analogous to the _ab_ _initio_ predictions of Gole and Hayes[11] for HO_2. In fact, the high degree of similarity is surprising since one intuitively suspects that LiO_2 should be much more ionic than HO_2 and therefore somewhat different in electronic structure. Billingsley and Trindle[8] have predicted the $^2B_2$ state to lie below the $^2A_2$ state, in apparent disagreement with our more complete calculations. We note that we have adopted the spectroscopic notation of Herzberg,[5] and that our $^2A_2$ ground state wave function correlates with a $^2A''$ wave function, which is anti-symmetric with respect to the plane of the molecule. Our predicted $^2A_2$ ground state geometry is in good qualitative agreement with that estimated from experimental data by Andrews.[7]

The $^2\Pi$ state, constrained to be of $C_{\infty v}$ geometry is predicted to lie only 1.2 kcal/mole above the $^2A_2$ state. The very small size of this energy difference suggests that the true equilibrium geometry of LiO_2 may be qualitatively $\begin{smallmatrix} Li \\ \diagdown \\ O\!-\!O \end{smallmatrix}$,

in analogy[9] with HO_2. This is in fact the prediction of Billingsley and Trindle.[8]
However, Andrews and coworkers have insisted that only an isosceles triangle
geometry is consistent with their experimental results. Therefore we carried out
the C_s calculations summarized in Table II. Perhaps the most important result
seen in Table II is that the energy of the $^2A''$ state becomes slightly higher in
going from the isosceles triangle to the adjacent C_s geometry. This seems to
establish the C_{2v} geometry as the true equilibrium. The analogous calculation
by Billingsley and Trindle yielded the opposite result. However the miniscule
nature of the energy diffences involved warns us to be cautious in our interpre-
tation. The proper procedure would be to compute the entire minimum energy path
connecting the C_{2v} and $C_{\infty v}$ minima.

From the standpoint of the dynamics of the Li + O_2 reaction, the most
important result found here is that the lowest potential energy surface, $^2A''$
is rather isotropic. That is, for any Li–O–O angle, the surface is attractive
by about the same degree. This result is quite different than that found
recently[17] for another attractive surface, F + Li_2. There the F – Li – Li
structure lies 30 kcal/mole higher in energy than $Li \diagup^{F}\diagdown_{Li}$. However, our LiO_2
result is analogous to that found by Clementi, Kistenmacher, and Popkie[18] for
the LiNC → LiCN system. they have used the term "polytopic" to describe the
Li – CN bond, in order to stress its equality in energy for substantially dif-
ferent Li – CN orientations.

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FOOTNOTES AND REFERENCES

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†Neshan Zovick Fellow.

††Alfred P. Sloan Fellow.

‡M. H. Fellow.

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Table I. Predicted Geometries and and Energies of the Lowest Two States

of LiO_2.

State	Total Energy (hartrees)	Relative Energy (kcal/mole)	R(Li–O) (Å)	θ(O–Li–O) (degrees)	R(O–O) (Å)
$^2B_2$	-157.061 18	14	1.76	46.5	1.39
$^2A_2$	-157.083 51	0.0	1.82	44.5	1.38
$^2\Pi$ (degenerate pair)	-157.081 59	1.2	1.62	–	1.35
Billingsley and Trindle[a]	-156.547	–	1.72	44.4	1.30
Experimental Estimate[b]	–	–	1.77	44.1	1.33

[a]Ref. 8.

[b]Ref. 7.

Table II. Calculations on the $^2A''$ State of LiO_2. Bond Distances are Tabulated in Bohr Radii (1 Bohr = 0.5292 Å).

Beginning Near the C_{2v} Equilibrium Geometry

R(Li-O)	R(O-O)	θ(Li-O-O)	E(hartrees)
3.454	2.600	67.9°	-157.083 489
		75°	-157.083 468
		090°	-157.078 435
		105°	-157.075 214
		120°	-157.074 165
		135°	-157.073 586
		150°	-157.072 849
		180°	-157.071 888

Beginning Near the $C_{\infty v}$ Equilibrium Geometry

R(Li-O)	R(O-O)	θ(Li-O-O)	E(hartrees)
3.05	2.56	180°	-157.081 587
		150°	-157.079 251
		135°	-157.076 691
		120°	-157.074 147
		105°	-157.073 418
		90°	-157.076 309
		75°	-157.07